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ABSTRACT

Early solar materials bear a variety of isotopic anomalies that reflect compositional differences deriving from distinct stellar nucleosynthetic processes. As shown in previous studies, the stepwise dissolution with increasing acid strengths of bulk rock carbonaceous chondrites liberates Cr with both excesses and deficits in ^{53}Cr and ^{54}Cr relative to the terrestrial standard. The magnitude of the ^{54}Cr variations within a meteorite decreases in the sequence CI1 > CR2 > CM2 > CV3 > CO3 > CK4 and correlates with the degree of metamorphism of each carbonaceous chondrite class. This study shows that the Tagish Lake meteorite presents the highest excesses in ^{54}Cr ever measured in a bulk silicate phase. According to this study, the Tagish Lake meteorite is composed of the least re-equilibrated material known at this time. The magnitude of ^{54}Cr variation decreases now in the following sequence: Tagish Lake (ungrouped CI2) > Orgueil (CI1) > Murchison (CM2) > Allende (CV2). Moreover, this study shows that excesses in ^{53}Cr relative to Earth can be interpreted as representing the extent of aqueous alteration on meteorite parent bodies. Finally, the high ^{54}Cr anomalies measured in this meteorite make Tagish Lake one of the major targets to decipher the host of these anomalies.

Key words: meteorites, meteors, meteoroids – nuclear reactions, nucleosynthesis, abundances – supernovae: general

1. INTRODUCTION

Chondritic meteorites such as carbonaceous chondrites host the most primitive components of the solar system. Hence, they provide important constraints on the chemical and isotopic composition of the solar nebula. Nucleosynthetic isotopic anomalies (excesses or deficits of an isotope measured relative to a terrestrial standard) have been discovered in meteorites, mainly in the iron-group elements (Ca to Zn) and are the greatest for their neutron-rich isotopes (^{48}Ca, ^{50}Ti, ^{54}Cr, ^{58}Fe, ^{64}Ni; e.g., Birck 2004). These nucleosynthetic anomalies are believed to reflect residual heterogeneities stemming from a variety of stellar sources and processes and bear evidence of incomplete mixing in the early solar system (e.g., Birck 2004; Clayton et al. 1973; Wasserburg et al. 2006).

Cr is of particular interest in the fact that besides the neutron rich effects on ^{54}Cr, ^{53}Cr is the decay product of ^{53}Mn, an extinct radionuclide, which has been shown to be present in the early solar system (e.g., Birck & Allègre 1985; Clayton 2003a). The isotopic compositions of ^{53}Cr and ^{54}Cr are reported as $\varepsilon^{53,54}$Cr values. The latter are defined as the deviation, in parts per 10,000 from the reference ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios (Birck & Allègre 1988).

The ^{53}Mn–^{53}Cr systematics is well suited to date the relative timescales of parent-body processes (e.g., Shukolyukov & Lugmair 2006; Trinquier et al. 2008b) or the time of formation of single crystal grains (e.g., Petitat et al. 2011). ^{54}Cr anomalies have been detected in presolar grains (Zinner 2005) and refractory inclusions (Birck & Allègre 1984; Papanastassiou 1986). ^{53}Cr and ^{54}Cr isotopic variations have also been measured in less refractory phases such as silicates (e.g., Rotaru et al. 1992).

The stepwise dissolution of carbonaceous chondrite whole rocks with increasing acid strengths exhibit deficits and excesses in ^{54}Cr relative to Earth (e.g., Dauphas et al. 2010; Moynier et al. 2010; Podosek et al. 1997; Qin et al. 2009; Rotaru et al. 1992; Trinquier et al. 2007). Moreover, Rotaru et al. (1992) demonstrated that the magnitude of the ^{54}Cr variations decreases in the sequence CI1 chondrites > CR2 chondrites > CM2 chondrites > CV3 chondrites > CO3 chondrites > CK4 chondrites and correlates with the degree of thermal metamorphism of each carbonaceous chondrite class. Hence, the Orgueil CI1 chondrite presents the highest ^{54}Cr anomalies ever measured in major mineral fractions, which is consistent with this meteorite being the least metamorphosed one (Lodders 2003). Finally, these authors explained the ^{54}Cr anomalies as reflecting the inhomogeneous distribution of distinct nucleosynthetic components in the solar system (e.g., Dauphas et al. 2010; Moynier et al. 2010; Podosek et al. 1997; Qin et al. 2009; Rotaru et al. 1992; Trinquier et al. 2007). However, the source of ^{54}Cr in the protoplanetary disk remains unknown since the carrier phase of the ^{54}Cr anomaly has not yet been identified (e.g., Dauphas et al. 2010; Moynier et al. 2010; Qin et al. 2009). This is presumably because it is fine grained and chemically labile.

Variations of ^{53}Cr relative to Earth measured during the stepwise dissolution of carbonaceous chondrites are two orders of magnitude smaller than those measured for ^{54}Cr (e.g., Dauphas et al. 2010; Moynier et al. 2010; Podosek et al. 1997; Qin et al. 2009; Rotaru et al. 1992; Trinquier et al. 2007). They have been interpreted as resulting from ^{53}Mn decay (Rotaru et al. 1992).

At the bulk rock scale, carbonaceous chondrites exhibit ^{53}Cr and ^{54}Cr excesses (e.g., Trinquier et al. 2007). The ^{53}Cr excesses measured for the different carbonaceous chondrite sub-groups correlate linearly with their respective elemental ^{55}Mn/^{52}Cr ratios. The corresponding ^{53}Mn/^{55}Mn ratios are $(8.5 \pm 1.5) \times 10^{-6}$ (Moynier et al. 2007; Shukolyukov & Lugmair 2006). These initial ratios are consistent with the best estimate initial ratio of the solar system (^{53}Mn/^{55}Mn ratio = $(9.7 \pm 1.1) \times 10^{-6}$)

Table 1
Chemical Procedure for the Stepwise Dissolution of Meteorite Whole Rocks

Stepwise Dissolution Procedure			
Leaching Step Number	Reagent	Procedure	Dissolved Minerals
Leach 1 (L1)	Acetic acid (17N)	2.5%, 30 min, 20°C	Easily soluble minerals (sulfates, sulfides, carbonates, metal, magnetite)
Leach 2 (L2)	Acetic acid (17N)	50%, 1 d, 20°C	
Leach 3 (L3)	HNO_3 (16N)	25%, 7 d, 20°C	
Leach 4 (L4)	HCl (6N) + HF (27N)	cc, 4 d, 100°C	Silicates
Leach 5 (L5)	HNO_3 (16N) + HF (27N)	cc, 10 d, 150°C	Refractory minerals
Whole rock	HNO_3 (16N) + HF (27N)	cc, 150°C	

Notes. The leaching procedure consists of five different leaching steps (1st column) during which major mineral phases of the meteorite whole rock are sequentially dissolved using acid mixes of increasing strengths. The molarities of the different acids used are reported (in brackets) in the 2nd column. The procedure followed in each step (proportion of acid mixed, duration of the dissolution procedure, and the temperature at which the dissolution took place) is represented in the 3rd column. The minerals dissolved at each step are indicated in the 4th column. min: minute; d: day.

calculated from the combination of ^{26}Al–^{26}Mg, ^{182}Hf–^{182}W, and ^{238}U–^{206}Pb data on chondrules and CAIs (Nyquist et al. 2009).

Here, we report ^{53}Cr and ^{54}Cr variations relative to Earth and the ^{52}Cr isotope measured during the selective dissolution of a fragment of the unique Tagish Lake meteorite to: (1) locate this meteorite in the carbonaceous chondrite Cr systematics, (2) address the significance of the excesses and deficits of ^{53,54}Cr relative to Earth, (3) investigate the origin of ^{54}Cr heterogeneity in the early solar system, and (4) refine the solar system initial ^{53}Mn/^{55}Mn ratio. The ungrouped carbonaceous chondrite breccia Tagish Lake was chosen because it presents unique petrological, mineralogical (Zolensky et al. 2002), and chemical (Pearson et al. 2001) characteristics, which place it between the CI1 chondrites and the CM2 chondrites. Moreover, its reflectance spectra seem to indicate that it would come from a D-type asteroid (Gounelle et al. 2008; Hiroi et al. 2001), which might be related to comets and sample a very pristine reservoir of the solar system (Gounelle 2011). A sample of Orgueil was measured in parallel for comparison with earlier studies.

2. EXPERIMENTAL METHODS

2.1. Tagish Lake

Tagish Lake is a unique ungrouped, anomalous C2 carbonaceous chondrite (Brown et al. 2000) and consists of two major lithologies, one carbonate-rich and another carbonate-poor that are thought to be genetically related (e.g., Zolensky et al. 2002). The Tagish Lake meteorite harbors (1) unusual petrologic and mineralogical characteristics in between those of CI1 and CM2 chondrites such as a fine-grained opaque matrix consisting mainly of phyllosilicates (intergrowth of serpentine and saponite), sulfides, and magnetites and within this matrix, the presence of altered CAIs and chondrules, isolated olivine grains, magnetite, carbonates, and Fe–Ni sulfides (Zolensky et al. 2002); (2) mineralogical indications of high degree of aqueous alteration such as the presence of altered CAIs, and of carbonates ranging in composition from pure calcite ($CaCO_3$) to siderite ($FeCO_3$) and magnesite ($MgCO_3$), the last two end-members not present in any other type of meteorites (Zolensky et al. 2002); (3) a bulk refractory lithophile element abundances similar to the one of CM2 chondrites, while bulk moderately volatile and volatile element abundances are between those of CI1 chondrites and CM2 chondrites (Mittlefehldt 2002); (4) an oxygen isotopic composition near those of CI1 chondrites and some metamorphosed carbonaceous chondrites but different from either of these and from the O-isotopic field of the CM2 chondrites (Engrand et al. 2001; Leshin et al. 2001); and (5) a bulk rock carbon isotopic composition distinct from those of CI1 chondrites and CM2 chondrites, although the carbonates in Tagish Lake have carbon isotopic compositions similar to those of these two meteorite groups (Grady et al. 2002). All these characteristics suggest that Tagish Lake is a new type of meteorite.

2.2. Digestion Procedure

Whole rock fragments of Orgueil and Tagish Lake of 0.32 g and 0.29 g, respectively, were first crushed into powder before being dissolved with a sequence of progressively stronger reagents using the chemical procedure described in Rotaru et al. (1992) and listed in Table 1. During the first two leaching steps (L1–L2), sulfates, carbonates, sulfides, and other easily soluble minerals were dissolved in dilute acetic acid. Their dissolution was then completed in step 3 (L3) by using dilute HNO_3. During leaching step 4 (L4), silicates were digested (HCL + HF conc.). Finally, refractory minerals, such as spinels, were attacked in leaching step 5 (L5) (HNO_3 + HF conc.). After each treatment, the sample was centrifuged and the supernatant was decanted with a pipette. The residue was then washed with water and centrifuged again. The washing procedure was repeated twice and the supernatants were collected to form the solution of that step. Subsequent to each dissolution step, small quantities of undissolved residue were removed for NanoSIMS 50 analyses. Additionally, a whole rock sample (0.05 g) of Tagish Lake was digested in a 1/1 mixtures of concentrated HF + HNO_3 acids at 150°C to investigate its bulk Cr isotopic composition.

The chemical separation of Cr was done according to Trinquier et al. (2008a).

2.3. Measurement Procedure

Cr is measured on a single degassed Re or W filaments with the addition of a mixture of colloidal SiO_2 and Boric acid (H_3BO_3). The detailed description of the TIMS measurements, data acquisition, and data correction is given in Trinquier et al. (2008a). After normalization to the terrestrial ^{52}Cr/^{50}Cr ratio, typical precisions obtained for Cr isotopic measurements are at the 10 ppm and 20 ppm level for the ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios, respectively. All data are expressed in $\varepsilon^{53,54}$Cr values, which are the relative deviation of the ^{53,54}Cr/^{52}Cr ratio from the terrestrial standard value expressed in one per 10,000. The Fe

Table 2
^{53}Cr and ^{54}Cr Isotopic Compositions, Mn and Cr Abundances and Elemental Ratios Measured for the Different Dissolution Steps for the Orgueil and Tagish Lake Carbonaceous Chondrites

Samples	Chemical Samples	ε^{53}Cr	ε^{54}Cr	^{55}Mn/^{52}Cr	Mn (ppm)	Cr (ppm)
Orgueil	Whole Rock	0.25 ± 0.03	1.56 ± 0.06	0.81 ± 0.02	2152	2897
	Leach 1 (L1)	2.00 ± 0.6	−5.13 ± 1.22	121.49 ± 1.03	498	9
	Leach 2 (L2)	1.00 ± 0.15	−6.08 ± 0.12	1.37 ± 0.04	444	365
	Leach 3 (L3)	0.04 ± 0.12	−6.78 ± 0.24	0.35 ± 0.01	419	1366
	Leach 4 (L4)	−0.62 ± 0.13	79.25 ± 1.81	0.57 ± 0.02	36	72
	Leach 5 (L5)	−0.84 ± 0.11	18.25 ± 0.28	0.10 ± 0.003	28	273
Tagish Lake	Whole Rock	0.53 ± 0.05	1.19 ± 0.15	1.69 ± 0.10	3361	2248
	Leach 1 (L1)	11.47 ± 0.58	−13.19 ± 1.4	82.6 ± 0.76	663	8
	Leach 2 (L2)	1.28 ± 0.26	−16.14 ± 0.47	3.34 ± 0.10	941	318
	Leach 3 (L3)	0.43 ± 0.10	−8.03 ± 0.16	1.02 ± 0.03	921	1025
	Leach 4 (L4)	−1.45 ± 0.37	139.01 ± 0.85	0.07 ± 0.002	4	67
	Leach 5 (L5)	−1.00 ± 0.17	13.80 ± 0.21	0.11 ± 0.003	16	188

Notes. Cr isotopic compositions were measured by TIMS (TRITON, Finnigan, Université Paris VI), whereas Mn and Cr abundances were measured on MC–ICP–MS (Neptune, Finnigan, Université Paris VI) in high-resolution mode to remove isobaric interferences on Cr species as described in Trinquier et al. (2008a). The ^{53}Cr and ^{54}Cr isotopic compositions are expressed in the ε-notation which is the relative deviation per 10,000 from the terrestrial standard. The ^{52}Cr/^{50}Cr ratio was used as a normalization ratio to correct for mass dependent instrumental fractionation (Shields et al. 1966). The iron isobaric interference on ^{54}Cr was controlled with ^{56}Fe. Error bars are 2σ; wr: whole rock. wr isotopic and elemental data for Orgueil were taken from Trinquier et al. (2007).

isobaric interference on ^{54}Cr was monitored on ^{56}Fe and using a measured ^{56}Fe/^{54}Fe ratio of 15.66 proved to be of negligible inference on the final precision. Procedural blanks of ~0.2 ng for Cr have negligible implication for the final results.

The Mn/Cr ratio was measured without chemical separation on an aliquot of each solution resulting from the dissolution procedure: steps L1–L5, solution of the bulk rock. This was done on a Neptune MC–ICP–MS in the medium resolution mode ($M/\Delta M = 4500$) to prevent polyatomic isobaric interferences. The measured Mn/Cr ratios in the samples are compared to standard solutions prepared at various Mn/Cr ratios in various matrixes. At the level of precision required for this study, the matrix effects resulting from the major elements of the various samples have negligible effects and the precision on the Mn/Cr ratio is better than 2%. Further details can be found in Trinquier et al. (2008a).

The elemental and isotopic compositions of each leaching step and of the whole rocks were measured twice and yielded identical values within analytical error.

3. RESULTS

This study confirms previous results and exhibits new features. Each fraction dissolved represents different mineral phases which all show positive and negative variations relative to Earth. At the mineral scale, stepwise bulk carbonaceous chondrite dissolutions have led to various ^{54}Cr and ^{53}Cr patterns with positive and negative anomalies relative to the terrestrial standard. Chromium isotopic results for the Orgueil and the Tagish Lake meteorites are detailed in Table 2. As listed in Table 2, Cr and Mn in Orgueil and Tagish Lake are mainly concentrated in the most easily dissolved fractions.

Whole rock. The ε^{53}Cr value measured for the whole rock of Tagish Lake is identical within error to that determined for Orgueil, whereas the ε^{54}Cr is higher in Orgueil than in Tagish Lake.

Anomalies in ^{54}Cr during mineral dissolution. Figure 1 illustrates the amplitude of the ε^{54}Cr heterogeneity among sequentially dissolved fractions of bulk rock carbonaceous chondrites measured in this study and in Murchison and Allende (Trinquier et al. 2007) for comparison. The pattern of isotopic data for Orgueil is similar to those obtained in previous studies (e.g., Dauphas et al. 2010; Podosek et al. 1997; Qin et al. 2009; Rotaru et al. 1992; Trinquier et al. 2007). The first three leaching steps (L1–L3) exhibit deficits in ^{54}Cr relative to Earth. These most easily dissolved fractions show a deficit relative to Earth ranging from -6ε for Orgueil to -16ε for Tagish Lake. In contrast, the highest ^{54}Cr excesses relative to the terrestrial standard are produced in the most chemically resistant fractions corresponding to the 4th and 5th leaching steps (L4–L5), which host excesses relative to the terrestrial standard rising up to 79ε for Orgueil and 139ε for Tagish Lake. With the exception of a magnetite enriched fraction from Orgueil (Podosek et al. 1997), this is the highest ^{54}Cr excess observed in one of the major mineral fractions of a meteorite (Figure 1).

Anomalies in ^{53}Cr during mineral dissolution. Figure 2 illustrates the ε^{53}Cr variations for Tagish Lake (this study), Orgueil (this study), and Murchison and Allende (Trinquier et al. 2007) for comparison. The pattern of isotopic data for Orgueil is similar to those obtained in previous studies (Dauphas et al. 2010; Podosek et al. 1997; Qin et al. 2009; Rotaru et al. 1992; Trinquier et al. 2007). The amplitudes of the variation are two orders of magnitude smaller than those measured for ^{54}Cr. Excesses in ^{53}Cr relative to Earth are concentrated in the chemically less resistant fractions, which possess the highest Mn/Cr ratios (Figure 2). Aside from dissolution step 1 (L1) and 4 (L4), Tagish Lake and Orgueil exhibit identical ε^{53}Cr values within uncertainties, which differ significantly from those measured in Murchison and Allende.

4. DISCUSSION

4.1. ^{54}Cr Anomalies at the Mineral Scale in Orgueil and Tagish Lake

Tagish Lake has several striking differences relative to the systematics of other carbonaceous chondrites. For the major minerals containing Cr, it displays both the highest excess and deficit in ^{54}Cr relative to Earth. The general trend from CI1 chondrites to CK4 chondrites is a decrease in the isotopic difference between leaching step 2 (L2) and leaching step 4

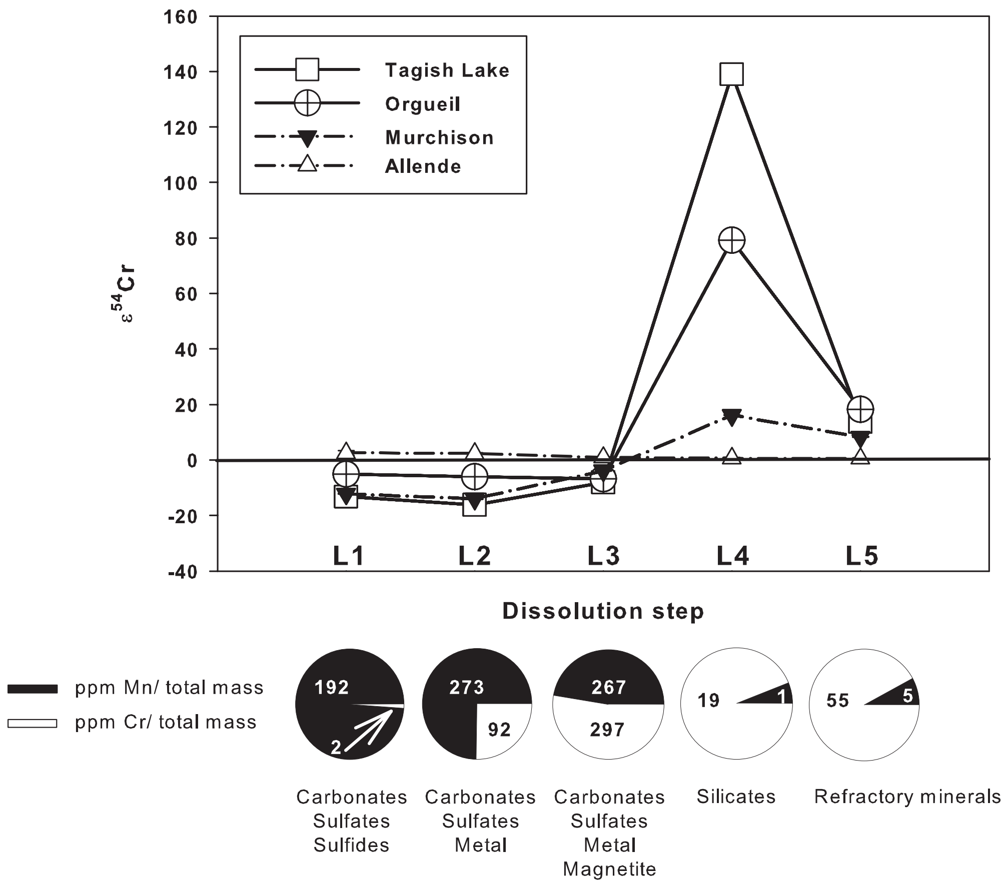

Figure 1. ^{54}Cr variations among sequentially dissolved fractions (L1–L5) of bulk rock carbonaceous chondrites. Tagish Lake (ungrouped C2 chondrite; this study): white square; Orgueil (CI1 chondrite; this study): crossed circle; Murchison (CM2 chondrite; Trinquier et al. 2007): black triangle pointing down; Allende (CV3 chondrite; Trinquier et al. 2007): white triangle pointing up. A clear pattern in the ^{54}Cr isotopic variations appears: Tagish Lake (ungrouped C2 chondrite); Orgueil (CI1 chondrite); Murchison (CM2 chondrite); Allende (CV3 chondrite). This pattern is attributed to metamorphism (Rotaru et al. 1992). Each pie chart represents the Mn and Cr abundances measured for the different dissolution steps of Tagish Lake relative to the total mass (0.29 g) analyzed. The abundances of Mn and Cr in the whole rock of Tagish Lake are higher than those obtained from the addition of the Mn and Cr abundances of the different leaching steps. This indicates an elemental fractionation during the Cr separation and purification chemistry. The major mineralogical phases dissolved during each digestion step are indicated.

(L4). This trend has been interpreted to be due to metamorphism (e.g., Rotaru et al. 1992). Since Tagish Lake displays the highest deficits (L2) and the highest excesses (L4) in ^{54}Cr relative to Earth, our results indicate that this meteorite may consist of the least metamorphosed matter ever analyzed.

In addition to parent body metamorphism, aqueous alteration may also have been a factor that controlled the amplitude of ^{54}Cr anomalies. The sequence of aqueous alteration for meteorite parent bodies is CI1 chondrites > CM2 chondrites > CR2 chondrites > CV3 chondrites > CO3 chondrites (e.g., Brearley 2006) and is identical to the general trend of the ^{54}Cr anomaly measured during meteorite whole rock dissolution (CI1 chondrites to CK4 chondrites). The fact that mineral phases such as carbonates, sulfates, and sulfides present ^{54}Cr deficits relative to Earth indicates that the fluid from which secondary minerals formed did not contain the carrier phase of the ^{54}Cr anomaly. Moreover, it shows that the carrier phase of the ^{54}Cr was not significantly altered during aqueous alteration. Finally, since Tagish Lake presents the highest ^{54}Cr anomalies ever measured in a meteorite, it represents a major target to determine the carrier phase of the ^{54}Cr anomaly. Indeed, it indicates that (1) Tagish Lake harbors a concentration of grains showing this ^{54}Cr anomaly larger than any other carbonaceous chondrites; (2) if the abundance of anomalous grains is the same as that of other carbonaceous chondrites, then the ^{54}Cr anomalies present in the sample are higher than those in Orgueil and the other carbonaceous chondrites; or (3) both aforementioned points are true.

4.2. *^{53}Cr Anomalies at the Mineral Scale of Carbonaceous Chondrites*

Tagish Lake presents a large excess of ^{53}Cr relative to the terrestrial standard and to the other meteorites studied so far after an attack by a very mild acid solution in the 1st leaching step (L1). In our opinion, this reflects the high proportion of carbonates in Tagish Lake (Zolensky et al. 2002) which buffers rapidly the dissolution medium at a close to neutral pH. Since carbonates are depleted in Cr, very little Cr is extracted.

The dissolution of carbonates, sulfates, and sulfides during the first three leaching steps (L1–L3) produces the highest ^{53}Cr excesses (Tagish Lake > Allende > Orgueil > Murchison), whereas the disintegration of the silicate portion in dissolution step 4 generates ^{53}Cr deficits relative to Earth (Tagish Lake > Orgueil > Murchison > Allende). Carbonates, sulfates, and sulfides are secondary minerals which precipitated from aqueous fluids on the meteorite parent bodies (e.g., Bullock et al. 2005; Endress & Bischoff 1996; Fredriksson & Kerridge 1988). It has been showed that the excesses of ^{53}Cr in single grains of different carbonate types are related to the decay of ^{53}Mn (e.g., deLeuw et al. 2009; Hoppe et al. 2007; Petitat 2010; Petitat et al. 2011). Hence, it seems reasonable to argue that ^{53}Cr excesses relative

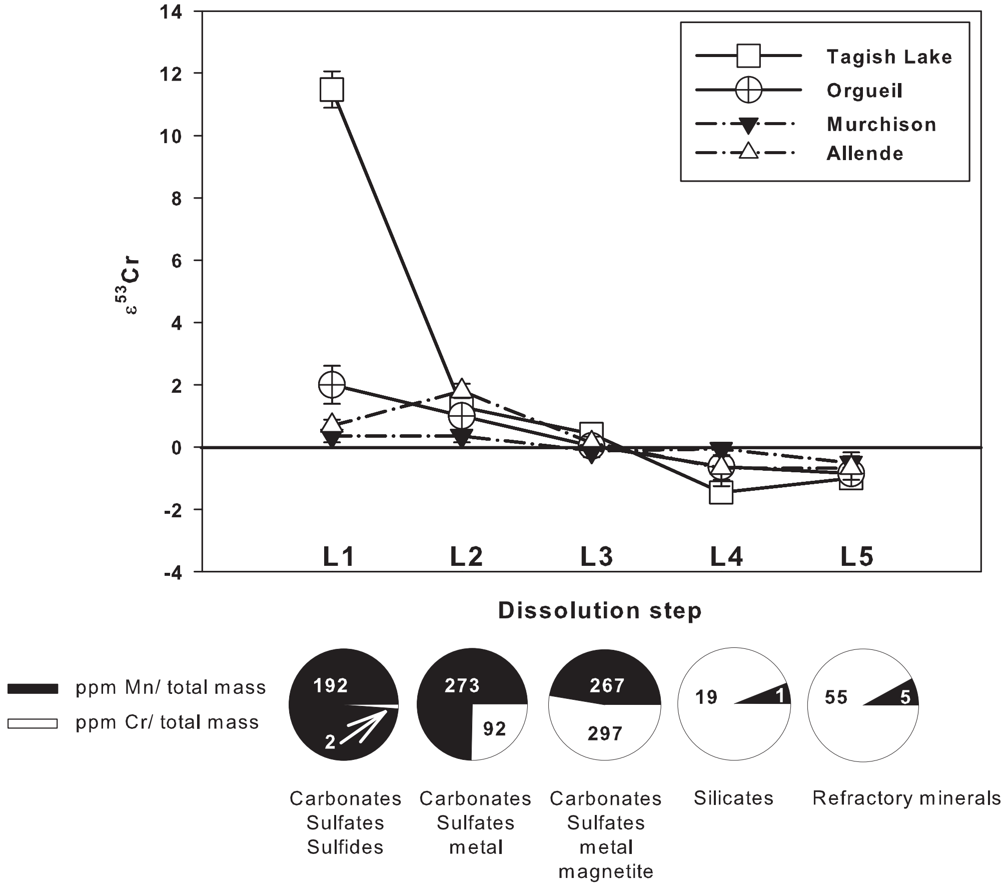

Figure 2. ^{53}Cr variations among sequentially dissolved fractions (L1–L5) of bulk rock carbonaceous chondrites. Tagish Lake (ungrouped C2 chondrite; this study): white squares; Orgueil (CI1 chondrite; this study): crossed circle; Murchison (CM2 chondrite; Trinquier et al. 2007): black triangle pointing down; Allende (CV3 chondrite; Trinquier et al. 2007): white triangle pointing up. The patterns obtained in this study are identical to those from previous studies. Acid non-resistant species (i.e., carbonates) release ^{53}Cr when dissolved. This is an inverse tendency to that observed for ^{54}Cr. Mn and Cr abundances relative to the total mass (0.29 g) measured for the different dissolution steps for Tagish Lake are represented in the pie charts and the major mineralogical phases dissolved are indicated.

to Earth measured in the first three leaching steps (L1–L3) are probably related to the leaching of minerals in which the ^{53}Mn decayed into ^{53}Cr.

The former presence of ^{53}Mn may be demonstrated by a linear correlation between the ε^{53}Cr values and their respective ^{55}Mn/^{52}Cr ratios measured for each dissolved fraction, which is not observed for Tagish Lake (Figure 3). This suggests that either the ^{53}Cr excesses are not linked to the radioactive decay of ^{53}Mn or if they are related to ^{53}Mn decay that the system is strongly disturbed. The latter hypothesis would be consistent with a system, in which the mineralogy is established in several episodes as shown in the recent ^{53}Mn–^{53}Cr ion probe data by Petitat (2010) and Petitat et al. (2011). In addition to these two hypotheses, it can also be argued that ^{53}Mn was heterogeneously distributed at the start of the solar system (Trinquier et al. 2008b; Gounelle & Russell 2005).

The zoom in Figure 3 shows that a linear correlation exists when combining the leaching steps 2–5 (L2–L5) and the whole rock. If interpreted as an isochron with some scatter due to secondary disturbance, this correlation yields an initial value of ^{53}Mn/^{55}Mn $= (8.4 \pm 0.9) \times 10^{-5}$. This is more than an order of magnitude higher than the most recent estimate of the initial solar system ^{53}Mn/^{55}Mn ratios (Trinquier et al. 2008b; Nyquist et al. 2009). The data of Tagish Lake are difficult to reconcile with other meteorite data without considering a thorough remobilization of the ^{53}Mn–^{53}Cr system by secondary processes such as aqueous alteration on the Tagish Lake meteorite parent body.

Finally, a comparison of Figures 1 and 2 shows that excesses of ^{53}Cr relative to Earth are measured in mineral fractions harboring ^{54}Cr deficits relative to Earth and vice versa (e.g., Podosek et al. 1997; Rotaru et al. 1992). This relation is probably linked to the Mn and Cr abundances present in the different leaching steps (Mn/Cr ratios), to mineralogical and petrological properties of the different mineral phases dissolved during the different steps, and also to time (decay of ^{53}Mn into ^{53}Cr), although it has been demonstrated that chronological information from leaching data are difficult to draw (Trinquier et al. 2008b).

4.3. Heterogeneity at a Whole Rock Scale: Tagish Lake

At the scale of bulk rock, carbonaceous chondrites display clearly resolved and variable ^{54}Cr excesses relative to Earth (Podosek et al. 1997; Qin et al. 2009; Rotaru et al. 1992; Trinquier et al. 2007) as shown in Figure 4. The ^{54}Cr anomaly determined for the Tagish Lake whole rock is lower than that from Orgueil but within error equals that of Murchison.

Each group of meteorites has different bulk O isotopic compositions. Trinquier et al. (2007) obtained a linear correlation between the bulk Δ'^{17}O values and the ^{54}Cr anomalies from different carbonaceous chondrites. The Δ'^{17}O values are defined as the δ^{17}O coordinate of the intercept between a mass

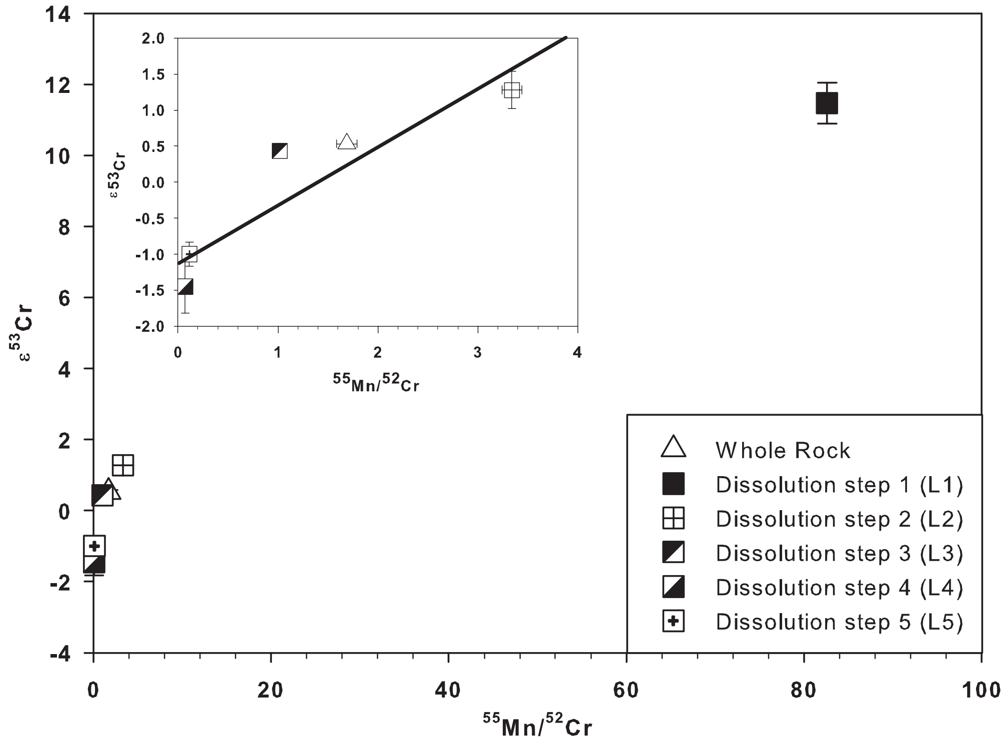

Figure 3. Plots of the ε^{53}Cr values vs. the elemental ^{55}Mn/^{52}Cr ratios measured for each dissolution step and for the whole rock of the Tagish Lake meteorite. As for previous studies, no linear correlation is observed, suggesting that the ^{53}Cr excesses are not linked to the radioactive decay of ^{53}Mn or if they are that the system is strongly disturbed. A linear correlation is observable when only considering leaching steps 2–5 (L2–L5) as presented in the zoomed diagram.

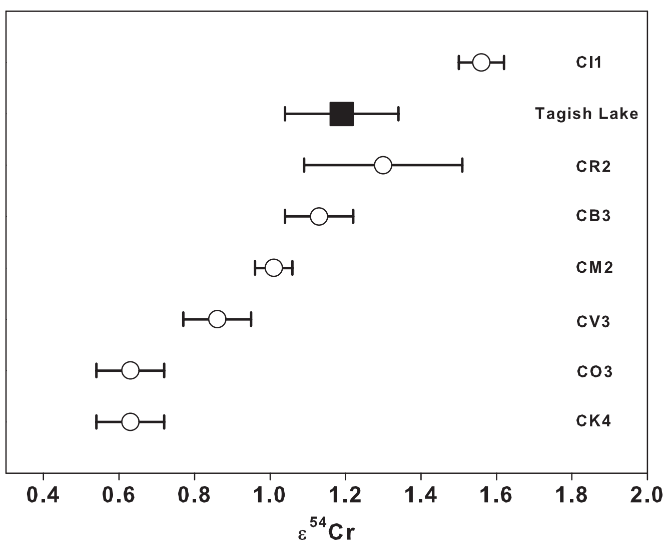

Figure 4. Plot of the ^{54}Cr excesses relative to Earth measured for different bulk rock carbonaceous chondrites. Tagish Lake data (black square) are from this study. Other carbonaceous chondrite data are from Trinquier et al. (2007).

fractionation line of slope 0.52 passing through each individual data point and the CC anhydrous mineral line (CCAM) of slope 1 (Trinquier et al. 2007). Since bulk O isotopic compositions are used to categorize meteorites, this linear correlation demonstrated that bulk ^{54}Cr anomalies could also be used to classify meteorites into different groups. The O and Cr isotopic data of the bulk Tagish Lake plot on this linear correlation in between those of the CI1 chondrites and CM2 chondrites but equals that of CR2 chondrites (Figure 5).

The excess in ^{53}Cr relative to Earth measured for the Tagish Lake whole rock is identical to that measured for CI1 chondrites. Tagish Lake is highly hydrated and contains two main lithologies, one carbonate-rich and another carbonate-poor. The sequential dissolution of bulk meteorite has shown that excesses in ^{53}Cr would appear in the solution of secondary minerals such as carbonates. Assuming a Tagish Lake carbonate grain contains 1 ppm Cr (Zolensky et al. 2002), a total sample mass of 0.05 g, and 2750 ppm Cr after dissolution, then the calculated mass of carbonate present in the analyzed sample of Tagish Lake is 36%. Therefore, the most probable lithology investigated in this study is the carbonate-rich lithology (~20% of carbonates; Zolensky et al. 2002). However, as only 0.05 g of Tagish Lake was digested, the sample might not be representative of the whole Tagish Lake parent body and a larger piece might carry information of both the carbonate-rich and the carbonate-poor lithologies. Nevertheless, the elemental ^{55}Mn/^{52}Cr ratio in the present data set is twice as high as in Yamashita et al. (2005) and most probably is at the origin of the elevated ^{53}Cr/^{52}Cr of the bulk rock reflecting the past presence of ^{53}Mn.

Figure 6 presents the linear correlation between the bulk rock ε^{53}Cr values and elemental ^{55}Mn/^{52}Cr ratios for different carbonaceous chondrites (Moynier et al. 2007; Shukolyukov & Lugmair 2006; Trinquier et al. 2008b). Our Tagish lake value deviates somehow from the internal bulk ^{53}Mn–^{53}Cr carbonaceous chondrite isochron (Moynier et al. 2007; Shukolyukov & Lugmair 2006; Trinquier et al. 2008b). However, since it presents the highest Mn/Cr ratio ever measured for a bulk meteorite, it contributes to better constrain the slope of this isochron. The resulting initial ^{53}Mn/^{55}Mn ratio = $(5.3 \pm 1.8) \times 10^{-5}$ is similar to that calculated by Birck & Allègre (1984) from Allende CAIs, but much higher than that determined by Nyquist et al. (2009) (^{53}Mn/^{55}Mn ratio = $(9.1 \pm 1.7) \times 10^{-6}$) combining ^{26}Al–^{26}Mg, ^{53}Mn–^{53}Cr, and ^{182}Hf–^{182}W measurements obtained from chondrules and CAIs from different carbonaceous chondrite and angrite meteorites. Our result is in agreement

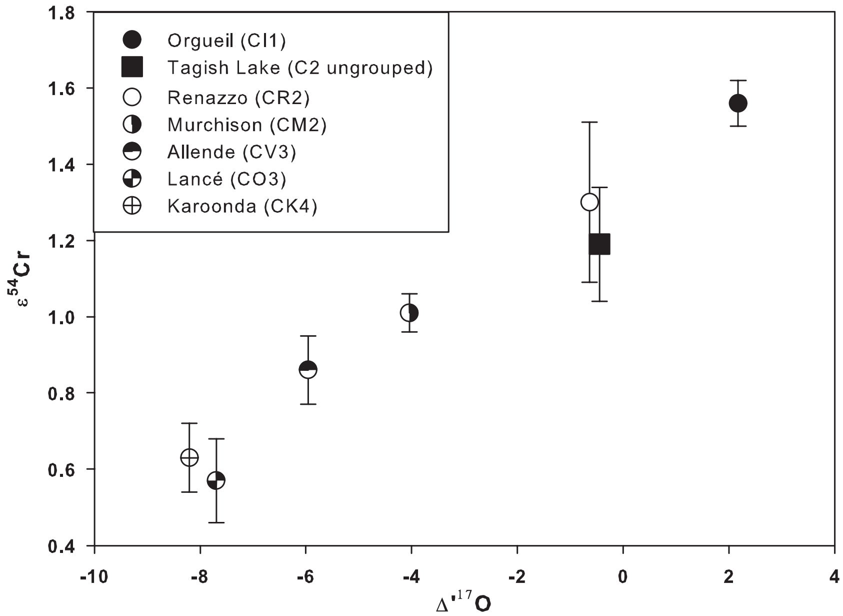

Figure 5. Plot of the ε^{54}Cr values vs. Δ'^{17}O for different carbonaceous chondrites. Tagish Lake (black square) plots on the linear correlation formed by the other carbonaceous chondrite. The oxygen isotopic composition of Tagish Lake was calculated from the average of the two values measured in Brown et al. (2000). The other oxygen isotopic compositions were taken from Clayton (2003b). The Δ'^{17}O were calculated following Trinquier et al. (2007).

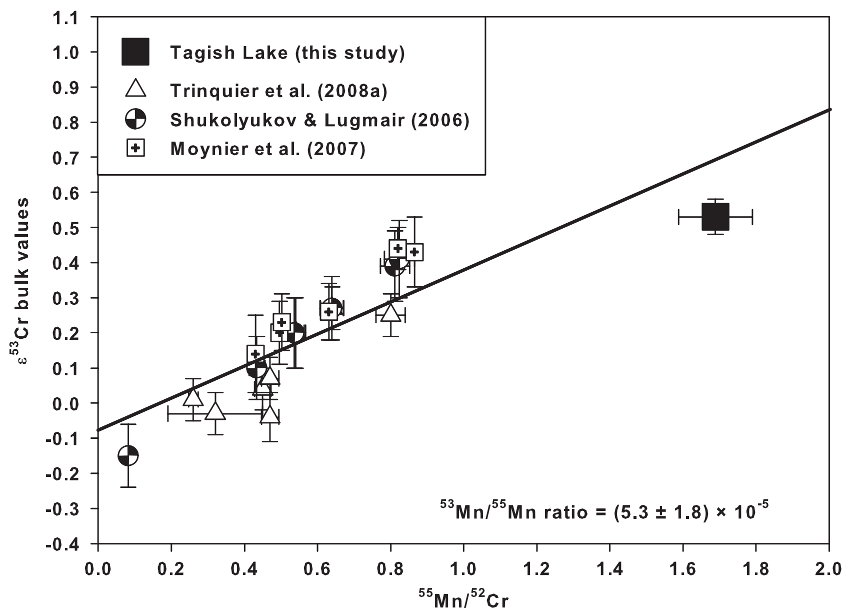

Figure 6. Plot of the ε^{53}Cr values and their respective ^{55}Mn/^{52}Cr elemental ratios measured for carbonaceous whole rocks. The high ^{55}Mn/^{52}Cr ratio measured in this study for the Tagish Lake (black square) whole rock permits to better approximate the ^{53}Mn/^{55}Mn initial ratio for the bulk rock carbonaceous chondrites.

with the hypothesis of Scott & Sanders (2009), who interpreted this whole-rock carbonaceous chondrite ^{53}Mn–^{53}Cr isochron as a mixing line between a volatile depleted (low Mn/Cr) and a volatile enriched CI1-like reservoir.

5. CONCLUSION

The ^{54}Cr excesses reported in this study for Orgueil are within the range of already published values. However, we report the highest ^{54}Cr excess so far for the silicate fraction of Tagish Lake. The high excess measured for Tagish Lake reinforces the fact that Tagish Lake consists of very pristine material (the most pristine of all according to this study). The magnitude of ^{54}Cr variation decreases now in the following sequence: Tagish Lake > Orgueil (CI1) > Murchison (CM2) > Allende (CV3). Finally, these large excesses make from Tagish Lake a major target for deciphering the carrier phase of the ^{54}Cr anomaly.

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